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## LIGHT INDUCED CHANGES IN THE OPTICAL PROPERTIES OF THIN As - S - Ge(Bi, Tl) FILMS

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In this paper we report results from studying changes in the optical properties of thin vacuum deposited films from the systems  $\text{As}_{40-x}\text{Ge}_x\text{S}_{60}$  ( $0 \leq x \leq 40$ ) and  $(\text{As}_2\text{S}_3)_{100-x}\text{Bi(Tl)}_x$  ( $0 \leq x \leq 15$ ) depending on the composition and conditions of evaporation and illumination to light. The optical transmission and reflection of thin layers deposited on BK-7 optical glass substrates have been measured in the spectral region of 350 - 1500 nm and the refractive indices and optical band gap  $E_g$  were calculated. It was found that the method of evaporation influences considerably the properties of thin chalcogenide films. The addition of Bi or Tl in  $\text{As}_2\text{S}_3$  leads to an increase in the refractive index while Ge causes its decreasing. The illumination of as-deposited films leads to an effect of photodarkening and decreasing in the optical band gap for As-containing films and photobleaching for As - Ge - S layers. Using  $\text{TRR}_m$  methods ( $R_m$  is the reflection of 100 nm thick films deposited on Si substrate), the thickness of very thin layers from the systems As - S and As - S - Ge have been determined to an accuracy of  $\pm 2$  nm. At the same time, the accuracy in the determination of the refractive index,  $n$ , was less than  $\pm 0.005$ . For the absorption coefficient,  $k$ , around the absorption edge, it was about  $\pm 0.01$ , using a combination of  $\text{TTR}_m$  and TR methods. A comparison between the results obtained from the spectrophotometric and ellipsometric measurements has been made.

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*Keywords:* Thin chalcogenide films, Optical constants, Photostructural changes

### 1. Introduction

Chalcogenide glasses are one of the most widely known families of amorphous materials and have been extensively studied for several decades, partly because of their interesting fundamental properties and partly because of their many potential applications in optical imaging, optical recording, infrared optics, and more recently, optical communications [1-5]. The determination of the optical constants is of great importance for understanding the mechanism of the optical processing and for their utilisation in practice. Because glassy  $\text{As}_2\text{S}_3$  is known as a stable stoichiometric binary compound, the systems As - S - Ge(Bi,Tl) have been chosen to continue our previous studies [6-9]. A number of works exist which trace the influence of composition and preparation conditions of thin films on the physico-chemical properties, and the changes in them induced by light. The structural changes in these materials are related to the change in their optical properties.

Various methods exist for determining the optical constants of thin films from the coefficients of transmission  $T$  and reflection  $R$ , or via their combination [10,11]. All these methods are based on the Swanepoel's method and different computer programs for calculation the optical constants and film thicknesses. As the film structure depends strongly on the conditions of evaporation there are some differences between the published data in the literature. The aim of the present work is to report results from a study of changes in the optical properties of thin As - S - Bi(Tl) films, depending on the composition and light illumination as well as to determine the optical constants of very thin As - S and As - Ge - S, using triple  $T$ ,  $R$ ,  $R_m$  methods [12, 13]. The major advantage of these is the simultaneous determination of  $d$  and the optical constants ( $n$ ,  $k$ ). The combination of triple and double TR methods results in a very accurate calculation of  $n$  and  $k$  [14, 15]. A comparison between the data, obtained by these methods and the ellipsometric measurements of the same films will be presented.

## 2. Experimental

The synthesis of the bulk samples as accomplished from starting substances (As, Ge, S, Tl and Bi) of 99.999 % purity, heated in a quartz ampoule at 970°C for 10 hours (As - Ge - S glasses) and at 870°C for 12 hours (As - S - Bi and As - S - Tl glasses). Thin films were deposited at room temperature onto optical glass substrates BK-7 and Si wafers in a high vacuum of  $10^{-3}$  Pa by thermal evaporation of previously weighed quantities of glasses with a residual in the boat. The composition of the bulk materials as well as the thin films was determined in a Scanning electron microscope with a X-ray microanalyser (Jeol Superprobe 733, Japan). (For bulks it was generally  $\approx 1$  at.% of the expected compositions). The exposure was carried out in air with a halogen lamp ( $20 \text{ mW/cm}^2$ ), for saturation times experimentally established for each composition. The film transmission  $T$  was measured with a spectrophotometer (CARY 05E, USA) to an accuracy better than  $\pm 0.1$  %, and the absolute reflections  $R_f$ ,  $R_b$  and  $R_m$  were measured with VW accessory to better than  $\pm 0.5$  % in the spectral range 350 to 1500 nm. The ellipsometric measurements were carried out at three angles of incidence of light (45, 48, 50 °), at  $\lambda = 632.8 \text{ nm}$ , using MAI-ellipsometry.

## 3. Results

### 3.1. Optical properties of thin As - S and As - Ge - S films

The optical constants of thin  $\text{As}_x\text{S}_{100-x}$  ( $28 \leq x \leq 45$ ) and  $\text{As}_{40-x}\text{Ge}_x\text{S}_{60}$  ( $0 \leq x \leq 40$ ) films deposited by thermal evaporation with a deposition rate 1.0-1.5 nm/s were calculated. The evaporation process was stopped when the film thickness was about 1000 nm with a residual in the boat. The refractive index and thickness were calculated from the transmission spectra using Swanepoel's method and a computer program developed by Konstantinov [13].

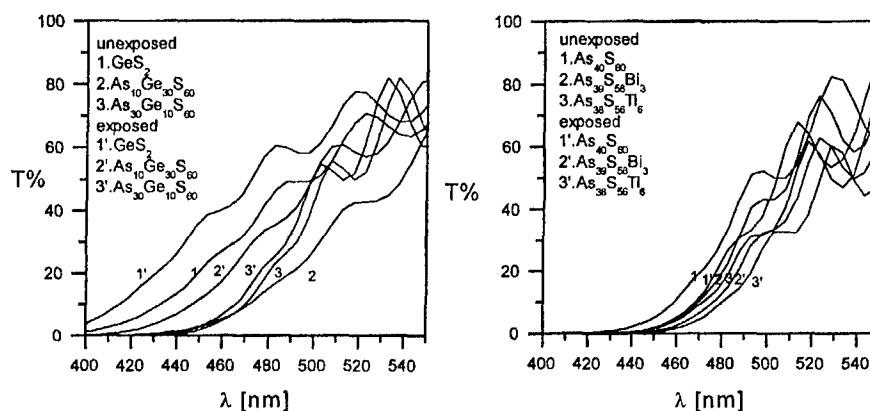


Fig. 1. Optical transmission of various chalcogenide thin films,  $T$ , vs. wavelength,  $\lambda$ , before and after illumination. This compositions are the ones exhibiting the largest light-induced changes in optical properties.

In Fig. 1 the plots of the optical transmission of various chalcogenide thin films versus wavelength, before and after exposure to light were presented. The compositions are the ones exhibiting the largest light-induced changes in the optical properties. It was found that after illumination the absorption edge for As - S - Bi(Tl) thin films shifts to the longer wavelengths (effect of photodarkening) while for the As - S - Ge system the effect was of photobleaching. In the system As - Ge - S the highest shift in the absorption edge ( $\Delta\lambda = -30$  % at  $T = 20$  %) and the refractive index ( $\Delta n = -0.07$ ) were found for the composition  $\text{As}_{10}\text{Ge}_{30}\text{S}_{60}$ . When Ge content increases the changes in the optical properties decrease. The thickness to an accuracy of  $\pm 1-3 \text{ nm}$  and the optical constants of chalcogenide films (100 nm thick) were determined by two triple ( $T$ ,  $R_f$ ,  $R_m$ ) and ( $T$ ,  $R_b$ ,  $R_m$ )

methods [12]. The subscripts  $f$  and  $b$  denote the light reflection from the film side and from the substrate (BK-7) side, respectively, while  $m$  represents the reflection of the same film deposited on a Si wafer. Table 1 shows the main data for the thickness of thin As - Ge - S films determined by UV-VIS-NIR spectrophotometry using T, R,  $R_m$  method and by ellipsometry. It seems that no difference in the thickness values of thin films from the investigated system.

Table 1. Data for the thickness of thin As-Ge-S films determined by UV-VIS-NIR spectrophotometry using a T, R,  $R_m$  method and by ellipsometry.

Composition	( T, R, $R_m$ ) method		Ellipsometric	
	$d_{unexp}$ [nm]	$d_{exp}$ [nm]	$d_{unexp}$ [nm]	$d_{exp}$ [nm]
As <sub>2</sub> S <sub>3</sub>	70 ± 1.0	68 ± 1.0	69.4 ± 0.1	69.5 ± 0.2
As <sub>30</sub> Ge <sub>10</sub> S <sub>60</sub>	95 ± 1.5	91 ± 2.0	93.6 ± 0.2	91.5 ± 0.1
As <sub>20</sub> Ge <sub>20</sub> S <sub>60</sub>	80 ± 1.0	85 ± 1.3	81.8 ± 0.2	86.2 ± 0.2
As <sub>10</sub> Ge <sub>30</sub> S <sub>60</sub>	52 ± 1.0	57 ± 1.0	53.6 ± 0.2	57.7 ± 0.3
GeS <sub>2</sub>	48 ± 1.5	50 ± 1.0	47.0 ± 0.2	49.7 ± 0.2

The most accurately calculated film thicknesses were used for the determination of the optical constants by double (T,  $R_f$ ) and (T,  $R_b$ ) methods, using the Newon-Raphson's iterative method [14]. For each of the applied methods for determining the optical constants and thickness, the absolute maximum errors were evaluated [15]. From the relationship  $d = f(\lambda) = \text{cons}$ , obtained by the triple methods, the physically corrected solutions for  $d$  were isolated. The determined by UV-VIS-NIR spectrophotometry optical constants depending on the film composition were compared with the data obtained on the same samples by MAI-ellipsometry (Table 2). It was found that the refractive index,  $n$ , had a maximum value for the As<sub>40</sub>S<sub>60</sub> films. After exposure to light to saturation  $n$  increases for all thin As<sub>x</sub>S<sub>100-x</sub> films while the thickness decreases. The highest change in  $n$  was observed for As<sub>40</sub>S<sub>60</sub> layers ( $\Delta n = 0.12$ ) (Fig. 2). The same dependence of  $n = f(\lambda)$  for unexposed and exposed thin As - S and As - Ge - S films was observed when (T,  $R_f$ ) and (T,  $R_b$ ) methods were used (Table 2).

Table 2. Data for the refractive index of thin As-Ge-S films with thickness of 1000 nm and below 100 nm at  $\lambda = 632.8$  nm obtained by UV-VIS-NIR spectrophotometry (1) and by ellipsometry (2).

Composition	Thin films 1000 nm thick				Thin films about 100 nm thick			
	Unexposed		Exposed		Unexposed		Exposed	
	1	2	1	2	1	2	1	2
As <sub>2</sub> S <sub>3</sub>	2.44	2.458	2.56	2.531	2.46	2.490	2.55	2.581
As <sub>28</sub> S <sub>72</sub>	2.33	2.428	2.40	2.417	2.33	2.414	2.42	2.456
As <sub>33</sub> S <sub>67</sub>	2.43	2.422	2.50	2.441	2.42	2.450	2.47	2.520
As <sub>45</sub> S <sub>55</sub>	2.43	2.456	2.52	2.553	2.45	2.454	2.54	2.553
As <sub>10</sub> Ge <sub>30</sub> S <sub>60</sub>	2.32	2.336	2.23	2.258	2.34	2.327	2.12	2.201
As <sub>20</sub> Ge <sub>20</sub> S <sub>60</sub>	2.35	2.369	2.30	2.280	2.34	2.388	2.23	2.281
As <sub>30</sub> Ge <sub>10</sub> S <sub>60</sub>	2.45	2.431	2.44	2.415	2.46	2.556	2.46	2.552
GeS <sub>2</sub>	2.15	2.131	2.11	2.096	2.12	2.131	2.02	2.027

The calculated values of the absorption coefficient,  $k$ , from the above mentioned methods were used for calculation of the absorption coefficient  $\alpha$  ( $\alpha = 4\pi k/\lambda$ ). Fig. 3 shows the plots of the  $(\alpha h\nu)^{1/2} = f(h\nu)$  dependence. When Ge was added to As<sub>2</sub>S<sub>3</sub> the optical band gap,  $E_g$ , increases for the unexposed layers. After exposure to light  $E_g$  increases and the biggest change  $\Delta E_g = 0.21$  eV was observed for thin film with composition As<sub>20</sub>Ge<sub>20</sub>S<sub>60</sub> (Table 3). The results for the composition dependence and the influence of the light obtained by refractive ellipsometry were in a good agreement with the data from the transmission spectrophotometry. It was found that  $k = 0$  when the optical constants were determined at 3 different angles of incidence of light on the sample and the calculated values of  $n$  at 45, 48 and 50° show that both unexposed and exposed thin As - S and As - Ge - S films are homogeneous.

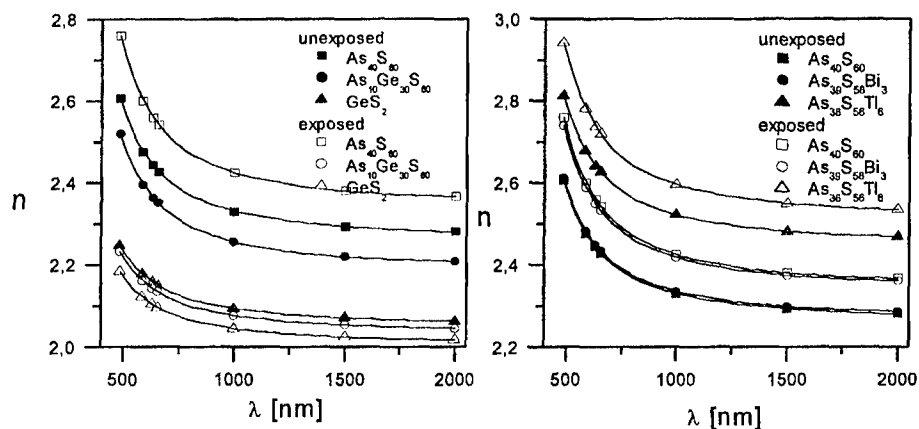


Fig. 2. Refractive index,  $n$ , vs. wavelength,  $\lambda$ , for various chalcogenide thin film samples before and after illumination. These compositions are the ones exhibiting the largest light-induced changes in optical properties.

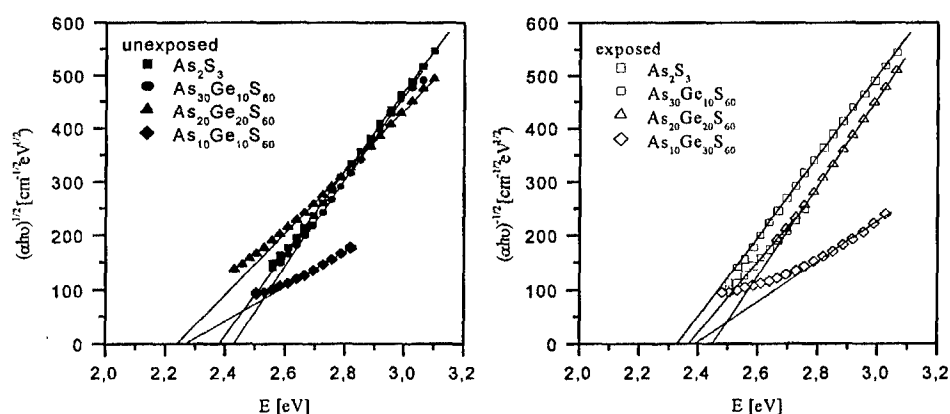


Fig. 3. Optical absorption edge  $(\alpha h\nu)^{1/2}$  vs. energy of photon ( $h\nu$ ) for unexposed and exposed thin As-Ge-S films

Table 3. Data for the optical band gap of unexposed and exposed thin As - Ge - S films.

Composition	$E_g$ unexp. [eV]	$E_g$ exp. [eV]	$\Delta E_g$ [eV]
$As_2S_3$	2.38	2.33	-0.05
$As_{30}Ge_{10}S_{60}$	2.42	2.49	+0.07
$As_{20}Ge_{20}S_{60}$	2.24	2.45	+0.21
$As_{10}Ge_{30}S_{60}$	2.27	2.39	+0.12
$GeS_2$	2.53		

### 3.2. Optical properties of thin As - S - Bi(Tl) films

Thin films (1000 nm thick) from the system As - S - Bi(Tl) were deposited by thermal evaporation of bulks with compositions  $As_{39}S_{58}Bi_3$ ,  $As_{38}S_{56}Bi_6$ ,  $As_{36}S_{54}Bi_{10}$ ,  $As_{39}S_{58}Tl_3$ ,  $As_{38}S_{56}Tl_6$  and  $As_{36}S_{54}Tl_{10}$ . It was found that the absorption edge of unexposed thin layers was shifted to longer

wavelength increasing the Bi or T content in  $\text{As}_2\text{S}_3$  (Fig.1). After exposure to light an effect of photobleaching occurred. The largest value of the shift of the absorption edge,  $\Delta\lambda$ , was observed for thin films with compositions  $\text{As}_{39}\text{S}_{58}\text{Bi}_3$  ( $\Delta\lambda = +15$  nm at  $T = 20\%$ ) and  $\text{As}_{38}\text{S}_{56}\text{Tl}_6$  ( $\Delta\lambda = +26$  nm at  $T = 20\%$ ). An increase in the Bi or Tl content leads to decreasing in the shift of the absorption edge.

From the transmission measurements we have calculated the refractive index of thin films from above systems. It was found that the values of  $n$  increases for the both systems (As - S - Bi and As - S - Tl) and the maximum changes in  $n$  was observed for thin layers with the same compositions -  $\text{As}_{39}\text{S}_{58}\text{Bi}_3$  ( $\Delta n = 0.10$ ) and  $\text{As}_{38}\text{S}_{56}\text{Tl}_6$  ( $\Delta n = 0.16$ ) (Fig.2). In the same time a decrease in the film thickness after exposure to light was found (for the composition  $\text{As}_{38}\text{S}_{56}\text{Tl}_6$   $\Delta d = -15$  nm).

In Table 4 the ellipsometrically determined values of  $n$  and  $d$  of thin As - S - Bi(Tl) films are shown. The calculated optical constants considerably differ comparing them with those determined by UV-VIS-NIR spectrophotometry for both unexposed and exposed thin films but the composition and exposure dependence was the same.

Table 4. Data for  $n$  and  $d$  for unexposed and exposed thin As-S-Bi(Tl) films.

Composition	$n_{\text{unexp}}$	$n_{\text{exp}}$	$d_{\text{unexp}}$ [nm]	$d_{\text{exp}}$ [nm]
$\text{As}_{39}\text{S}_{58}\text{Bi}_3$	2.477	2.450	1014	978
$\text{As}_{38}\text{S}_{56}\text{Bi}_6$	2.367	2.353	1118	1117
$\text{As}_{39}\text{S}_{58}\text{Tl}_3$	2.367	2.493	1036	1037
$\text{As}_{38}\text{S}_{56}\text{Tl}_6$	2.712	2.832	930	877
$\text{As}_{36}\text{S}_{54}\text{Tl}_{10}$	2.599	2.632	1073	1044

### 3.3. Optical absorption of thin As - S - Bi(Tl) films

In the case of the amorphous chalcogenide semiconductors, the optical absorption coefficient,  $\alpha$ , changes rapidly for the photon energies comparable to that of the band gap,  $E_g$ , giving rise to an absorption edge. Three regions can be distinguished: at the largest photon energies ( $\alpha \geq 10^4$  cm<sup>-1</sup>), in the region of the edge itself ( $10 < \alpha < 10^4$  cm<sup>-1</sup>) and at the lowest photon energies ( $\alpha \leq 10$  cm<sup>-1</sup>). The region with high absorption is characterised with interband transitions between valence and conduction bands, while in the last region transitions between (defect) states in the gap and the bands take place [16].

At the highest values of the absorption coefficient,  $\alpha$ , when the condition  $\alpha d > 1$  takes place, the absorption coefficient,  $\alpha$ , should be calculated from the equation

$$T = (1 - R)^2 \exp(-\alpha d), \quad (1)$$

where  $T$  is the transmittance,  $R$  is the reflectance,  $\alpha$  is the absorption coefficient and  $d$  is the film thickness.

Under certain conditions, the absorption coefficient in the region ( $10^4 \leq \alpha \leq 10^5$  cm<sup>-1</sup>) exhibits a power-law dependence on photon energy  $h\nu$  if the densities of states in the valence and conduction bands also have a power-law energy dependence in the vicinity of the gap. In the special case, where both valence and conduction band edges have a parabolic shape. According to Mott and Davis the absorption coefficient is connected with the photon energy by the equation

$$(\alpha h\nu) = B (h\nu - E_g)^2, \quad (2)$$

where  $B$  is a substance parameter,  $h$  is Plank constant and  $\nu$  is the frequency. Usually  $B$  depends on the width of the localised states in the band gap, which existing is due to the homeopolar bonds in the chalcogenide glasses. Thus  $Tauc$  plots of  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  should be linear and extrapolate to values of the (optical) gap,  $E_g$ .

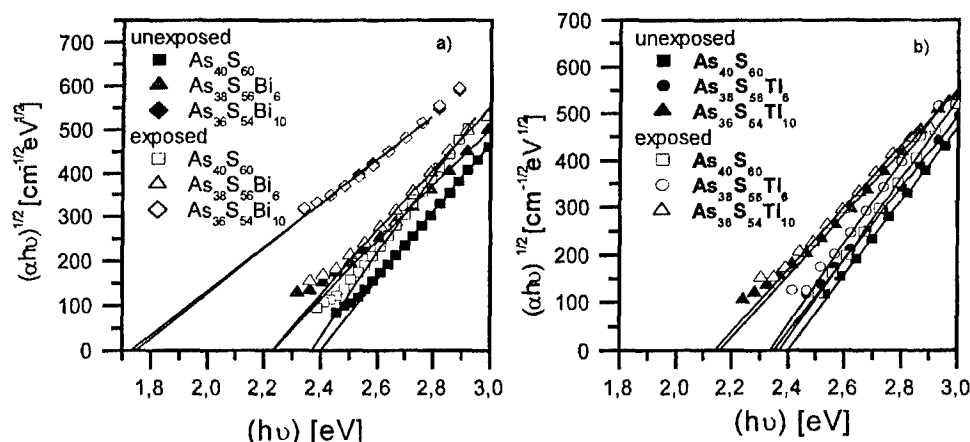


Fig. 4. Optical absorption edge  $(\alpha hv)^{1/2}$  vs. energy of photon  $(hv)$  for unexposed and exposed thin As-S-Bi(Tl) films.

Figs. 3 and 4 represent plots of  $(\alpha hv)^{1/2}$  vs.  $hv$  for various unexposed and exposed thin films from the systems As-Ge-S and As-S-Bi(Tl). It was found that the optical band gap decreases for as-deposited As-S thin films increasing the As content ( $E_g = 2.53$  eV for  $As_{28}S_{72}$  and  $E_g = 2.36$  eV  $As_{45}S_{55}$  (Fig.3). After exposure a decrease in  $E_g$  occurred and the highest change was for thin  $As_{45}S_{55}$  films ( $\Delta E_g = -0.05$  eV). This decrease in the optical band gap could be connected with the increase in the constant B, which according to Mott and Davis is due to the increasing in the structural ordering.

The plots of  $(\alpha hv)^{1/2}$  vs.  $hv$  for unexposed and exposed As-S-Bi films depending on Bi content are shown in Fig. 4a. In the range of high absorption the linear dependence retains and it is evident that the absorption edge shifts to lower photon energies as the Bi content increases. The band gap for the unexposed films decreases from  $E_g = 2.39$  eV for  $As_{40}S_{60}$  to  $E_g = 2.06$  eV for  $As_{36}S_{54}Bi_{10}$ . For as-deposited As-S-Tl films the optical band gap decreases to 2.16 eV for thin  $As_{36}S_{54}Tl_{10}$  films (Fig. 4b) [9]. In the same time the slope of the absorption coefficient decreases because of a decrease in disordering. The values of B decreases from  $777 \text{ cm}^{-1/2} \text{ eV}^{1/2}$  for  $As_{39}S_{58}Bi_3$  to  $563 \text{ cm}^{-1/2} \text{ eV}^{1/2}$  for the composition  $As_{36}S_{54}Bi_{10}$ . After exposure of thin As-S-Bi(Tl) films, the absorption edge is shifted to longer wavelengths - an effect of photodarkening is observed. The optical band gap decreases for both systems and the largest changes were found for composition  $As_{39}S_{58}Bi_3$  -  $E_g = 0.04$  eV (Fig. 4a). The decrease in the band gap with an increased Bi or Tl content occurs because the latter creates localised states in the band gap.

#### 4. Discussion

It should be noted that thin As-containing chalcogenide films represent inorganic polymers with specific branched polymer structure. According to some authors, the as-deposited As-S and As-S-Me layers are a heterogeneous mixture of structural units of the type  $As_2S_3$ ,  $As_4S_3$ ,  $As_4S_4$ ,  $As_4S_8$ ,  $TlAsS_2$ ,  $Tl_3AsS_3$  or  $BiS_3$ . In  $As_2S_3$  glasses the  $AsS_3$  trigonal pyramidal units are linked by the sulphur atoms. It was suggested that the addition of  $Tl_2S$  to  $As_2S_3$  glasses breaks some As-S-As bridges in order to form new bonds between electrically charged ions. On illumination, polymer-destructive changes occur leading to the weakening of some bonds and to strengthening of others. The existence of structural changes in such chalcogenide films on illumination is supported by changes in their optical properties (the shift in the absorption edge, the refractive index and the optical band gap). The addition of Tl or Bi to thin As-S-Bi(Tl) films leads to the increase of the refractive index and decrease of  $E_g$ . Adding Tl to  $As_2S_3$  the average bond strength of the compound decreases and

hence  $E_g$  will decrease. For better understanding the nature of the photostructural changes we need some IR and Raman investigations.

## 5. Conclusions

Bulk glasses from the systems As - S - Ge(Bi, I) have been synthesized. The results of the X-ray microanalysis performed that the compositions of the bulks samples as well as thin As - S - Ge films are very close to the expected compositions. Some differences were observed in the compositions

As - S - Bi(Tl) films connected with the evaporation conditions. From the transmission and ellipsometric measurements the optical constants have been determined and the influence of the composition and light illumination has been demonstrated. For their precise calculation it is necessary to utilise both transmission and ellipsometric measurements. The results confirm for the first time the viability of the double and triple methods used for determining the optical constants of very thin vacuum deposited homogeneous As - S and As - Ge - S films to a very high accuracy. The great changes in the optical properties of some of the investigated chalcogenide films make possible their application as optical recording materials.

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